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# 1,2-Dicyclopropylethyne and (Cyclopropylethynyl)cyclobutane from an Efficient Synthesis of 1,2-( $\omega$ -Haloalkyl)ethynes and 1-Cycloalkyl-2-( $\omega$ -haloalkyl)ethynes

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**Abstract:** Lithium acetylides, generated from terminal acetylenes with  $n$ -BuLi in THF at  $-70$  °C, react chemoselectively with  $\omega$ -haloalkyl tosylate in the presence of 10 mole % of  $\text{Bu}_4\text{NI}$  at  $70$  °C to furnish  $\omega$ -haloalkyl acetylides in very good yields. The  $\omega$ -haloalkyl acetylides undergo intramolecular alkylation with LDA to provide dicycloalkyl-ethynes.

**Key words:** Chemoselective alkynylation,  $\text{Bu}_4\text{NI}$  catalyst,  $\omega$ -haloalcohols,  $\omega$ -haloalkyl alkynes, intramolecular cyclization

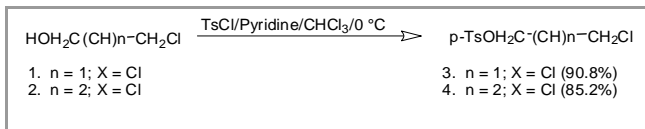
The classic methods for the synthesis of terminal/internal alkynes involve the alkynylation of alkylhalide with metal acetylide<sup>1</sup> as well as base promoted dehydrohalogenation<sup>2</sup> of vicinal dihalide/vinyl halide. Programmatically, our research interest is directed towards 1,2-dicycloalkylacetylides having ring strain cyclopropyl and / or cyclobutyl groups. The synthesis of 1,2-dicycloalkylalkyne can be achieved either by generation of the acetylene bond in an appropriate precursor having a dicycloalkyl group or by constructing the cycloalkyl group via intramolecular alkylation of the appropriate 1,2-  $\omega$ -haloalkyl acetylenic compound. The literature synthesis of 1,2-dicyclopropylethyne involves the internal alkylation of 1,2-  $\omega$ -haloalkylethyne forming cyclopropyl group<sup>3</sup> and via rearrangement<sup>4</sup> or elimination<sup>5</sup> of a suitable cyclopropyl precursor to generate the acetylenic bond. The internal carbocyclization approach is more promising as it does not require any exotic starting materials and is largely free from any by-products. Meijere et al. introduced cyclopropyl rings via intramolecular alkylation<sup>3</sup> of the 1,8-dichlorooct-4-yne<sup>8</sup> using lithium diisopropylamide (LDA). However, the alkynylation of dihaloalkane with metal acetylide suffers from low yield as is evident from the reported synthesis of 5-chloropent-1-yne (**5**, 57%)<sup>9</sup> and 1,8-dichlorooct-1-yne (**9**, 36%).<sup>8</sup> The synthesis of the parent 1,2-dicyclobutyl-ethyne is not reported in the literature. However, Handy and Benson reported<sup>6</sup> the synthesis of bis-(tetrahalocyclobutyl)ethyne. The condensation of divinylethyne with tetrafluoro- and chlorotrifluoroethylene furnishes bis(tetrafluorocyclobutyl)ethyne at high temperature ( $\sim 150$  °C) in a sealed vessel. Salaun, Fadel and Conia reported<sup>7</sup> the synthesis of a (cyclopropylethynyl)cyclobutane derivative, 2-(cyclopropylethynyl)-cyclobutanone, via ring enlargement of the 1-(3-cyclopropyl-1-hydroxyprop-2-ynyl)cyclopropanol.

$\omega$ -Haloalkylethynes are required for internal cyclization to furnish dicycloalkylethynes. Conventionally, alkynylation of haloalkanes is carried out using metal acetylides in

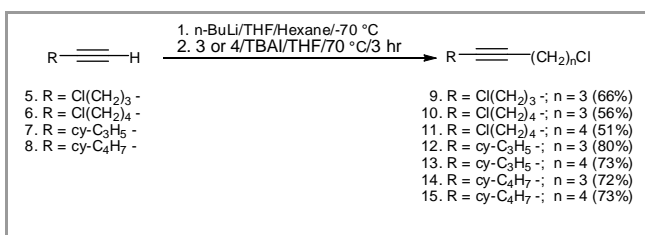
liquid  $\text{NH}_3$  having hexamethylphosphoramide (HMPA)<sup>10</sup> or  $N,N'$ -dimethylpropyleneurea (DMPU)<sup>11</sup> as a co-solvent. Chong and Buck<sup>12</sup> reported the dramatic effect of utilizing a catalytic amount (10 mol %) of sodium iodide (NaI) or tetrabutylammonium iodide ( $\text{Bu}_4\text{NI}$ ) for the reaction of lithium acetylides with primary halides ( $\text{X} = \text{Br}$  or  $\text{Cl}$ ) to form  $\omega$ -haloalkyl acetylides in tetrahydrofuran (THF). In contrast, the reaction is very sluggish and incomplete when conducted in only THF. Furthermore, the reaction in THF solution eliminates health hazard associated with the HMPA or DMPU and/or the inconvenience carrying out reaction in liquid  $\text{NH}_3$ . The difference in reactivity between triflate and bromide groups for the  $\text{S}_{\text{N}}2$  alkynylation of  $\omega$ -bromoalkyl triflates led Chong et al.<sup>13</sup> to synthesize unsymmetrical non-conjugated diynes. Thus, chemoselective monoalkynylation of  $\omega$ -bromoalkyl triflates with alkynyllithium followed by another alkynylation of the resulting bromoalkyne with alkynyllithium in the presence of 10 mol % NaI or  $\text{Bu}_4\text{NI}$  leads to unsymmetrical non-conjugated diynes. We report here an efficient and economical synthesis of  $\omega$ -chloroalkyl acetylides (**9-15**) along with 1,2-dicycloalkylethynes i.e. 1,2-dicyclopropyl-ethyne (**16**) and (cyclopropylethynyl)-cyclobutane (**17**).

$\omega$ -Haloalkylcycloalkyl or 1,2-di ( $\omega$ -haloalkyl) alkynes, precursors for 1,2-dicycloalkylacetylides, are required for internal carbocyclization. The alkynylation reaction of 1-bromo-3-chloropropane/1-bromo-4-chlorobutane is very sluggish and incomplete in THF. However, the reaction in the presence of 10 mol %  $\text{Bu}_4\text{NI}$  results in an inseparable mixture of corresponding bromo- and chloroalkylalkynes. Taking advantage of chemoselectivity between the tosylate and the chloro group,  $\omega$ -chloroalkyl tosylates (**3** or **4**) are used for the  $\text{S}_{\text{N}}2$  alkynylation reaction to avoid mixture formation.

**Tosylation of  $\omega$ -Haloalkyl Alcohols (**1** & **2**):** The 3-chloropropyl-4-methylbenzenesulfonate (**3**)<sup>14</sup> and 4-chlorobutyl-4-methylbenzenesulfonate (**4**)<sup>15</sup> are prepared from 3-chloropropanol (**1**) and 4-chlorobutanol (**2**) respectively by using alcohol/ tosyl chloride/ pyridine (1: 1.5: 2) developed<sup>16</sup> by Kabalka et al. (**Scheme-1**). The yield of **3** improves from 76% to 95%.

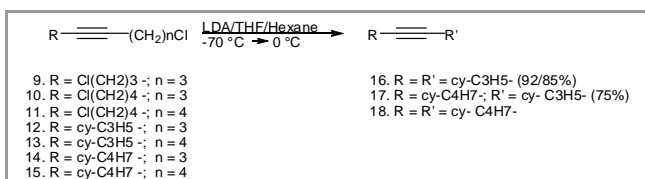
**Scheme 1: Tosylation of  $\omega$ -Haloalkyl Alcohols**

**Chemoselective alkynylation of  $\omega$ -chloroalkyl tosylates (3 & 4):** Whitley et al. performed<sup>14</sup> the alkynylation of **3** using stoichiometric quantity of  $n\text{-Bu}_4\text{NBr}$  in THF. Herein, we adopt the catalytic methodology<sup>12,13</sup> developed by Chong and coworkers. The Lithium acetylides generated *in situ* from alkynes **5-8** and  $n$ -butyllithium (2.5 M hexane  $n\text{-BuLi}$ ) in THF at  $-70^\circ\text{C}$ , react with  $\omega$ -chloroalkyl tosylate **3** or **4** in the presence of 10 mole % of  $n\text{-Bu}_4\text{NI}$  at  $70^\circ\text{C}$ , to produce corresponding single  $\omega$ -chloroalkylated acetylenes **9-15** in the range of 50-80% yield (**Scheme-2**).

**SCHEME 2: Alkynylation of  $\omega$ -Haloalkyl Tosylates**

**Intramolecular cyclization of  $\omega$ -Haloalkylated Acetylenes (9-15):** An intramolecular cyclization of  $\omega$ -haloalkylated acetylene by generating a carbon nucleophile adjacent to an acetylenic bond with LDA, was adopted to furnish 1,2-dicycloalkylethyne.

**1,2-Dicyclopropylethyne (16):** Treatment of 1,8-dichloro-oct-4-yne (**9**) or (5-chloropent-1-ynyl)cyclopropane (**12**) with an appropriate quantity (vide experimental) of freshly prepared LDA, generates 1,2-dicyclopropylethyne (**16**) in 92% & 85% yield respectively (**Scheme-3**).

**Scheme 3: Intramolecular cyclization of  $\omega$ -Haloalkylated Acetylenes**

**(cyclopropylethynyl)cyclobutane (17):** The exposure of (5-chloro-1-ynyl)cyclobutane (**14**) to 3.1 equivalents of LDA supplies 1-cyclobutyl-2-cyclopropylacetylene (**17**) in 75% yield. However, the treatment of 1,9-dichloro-4-nonyne (**10**) with 4.1 equivalents of LDA yields (6-chlorohex-1-ynyl)cyclopropane (**13**) at low temperature ( $\sim 0^\circ\text{C}$ ). The 6-chlorohex-1-ynyl moiety in **13** fails to cyclize with LDA to furnish **17** at  $0^\circ\text{C}$ . Warming the reaction mixture to room temperature ( $\sim 22^\circ\text{C}$ ) affords a complex mixture of products after workup of the reaction.

**1,2-Dicyclobutylacetylene (18):** The treatment of **11** or **15** with an appropriate quantity of LDA fails to produce 1,2-dicyclobutylacetylene (**18**). Our attempts to cyclize the 6-chlorohex-1-ynyl group to a cyclobutyl group using a Hauser base<sup>17</sup> at an elevated temperature ( $\sim 77^\circ\text{C}$ ) as reported in the literature<sup>18</sup> was also unsuccessful. These results further corroborate the earlier findings<sup>19</sup> of the non-competitiveness of cyclobutyl group formation with dehydrohalogenation and allene-acetylene rearrangement.

In conclusion, we have developed a very efficient and cost effective synthesis for the alkynylation of  $\omega$ -chloroalkyl tosylates. The yield of 1,8-dichloro-4-octyne, precursor for 1,2-dicyclopropylethyne, has been improved dramatically by a catalytic amount of  $\text{Bu}_4\text{NI}$  (vide supra). The yield of 1,2-dicyclopropylethyne is further improved using 4.1 vs. 2.1 equivalents of LDA as reported<sup>3</sup> in the literature. The alkynylation and intramolecular alkylation methodologies is successfully applied towards the synthesis of hybrid (cyclopropylethynyl)cyclobutane (**17**).

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker-Spectrospin 400 Ultrashield™ instrument. The proton and carbon chemical shifts (ppm) were referenced to the corresponding solvent peaks. A Nicolet 6700 FT-IR spectrophotometer was used to record IR spectra. Elemental analyses were determined on Perkin Elmer 2400 Series II CHNS/O analyzer. Analytic samples were prepared by a freeze-thaw distillation.

**General Procedure for Tosylation of  $\omega$ -Chloroalkyl Alcohols:**

$p$ -Toluenesulfonyl chloride (1.5 equivalents) was added to a cold chloroform solution ( $\sim 4^\circ\text{C}$ ) of  $\omega$ -haloalkyl alcohols (1 equivalent) and pyridine (2 equivalents) in small portions while stirring. Thin layer chromatography (TLC) was utilized to monitor the reaction mixture until completion. The reaction mixture was then quenched with water and extracted with ether. The organic layer was washed successively with aq. 2N HCl, 5% aq.  $\text{NaHCO}_3$  and water till aqueous layer was neutral. The organic layer was dried over anhydrous  $\text{MgSO}_4$ . After removal of solvent, the crude tosylate was charged onto a silica gel column. Excess of  $p$ -toluenesulfonyl chloride was removed by eluting the column with 10% ethylacetate-hexane. Further elution of the column with 15% ethyl acetate-hexane yielded  $\omega$ -haloalkyl tosylates.

**3-Chloropropyl-4-methylbenzenesulfonate (3):**

Adopting the above general procedure, 3-Chloropropyl-4-methylbenzenesulfonate (**3**) was prepared from 3-Chloropropanol (10.63 g, 112.4 mmol) (**1**), pyridine (18.22 g, 18.6 mL, 230.3 mmol),  $p$ -toluenesulfonyl chloride (32.65 g, 171.3 mmol) and chloroform (56 mL). The reaction was complete in 2.5 h (monitored by TLC). The reaction was quenched with ether (180 mL) and water (60 mL).

Yield: 25.46 g, 90.8%; B.P. =  $100\text{--}130^\circ\text{C}/0.02\text{--}0.03$  Torr

IR (neat): 2970, 1598, 1364, 1189, 1177, 1097,  $936\text{ cm}^{-1}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.80 (2H, d,  $J = 8$  Hz, ArH), 7.37 (2H, d,  $J = 8$  Hz, ArH), 4.2 (2H, t,  $J = 6$  Hz,  $-\text{CH}_2\text{OSO}_2\text{Cl}$ ), 3.6 (t,  $J = 6$  Hz,  $-\text{CH}_2\text{Cl}$ ), 2.4 (3H, s,  $\text{ArCH}_3$ ), 2.1 (2H, q,  $J = 6$  Hz,  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ ).

$^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  145.2, 132.9, 130.1, 128.1, 67.0, 40.5, 31.9, 21.9.

Anal. Calcd for  $\text{C}_{10}\text{H}_{13}\text{SO}_3\text{Cl}$ : C, 48.29; H, 5.27. Found: C, 48.24; H, 5.23.

**4-Chlorobutyl-4-methylbenzenesulfonate (4):**

Using 4-Chloro-1-butanol (9.33 g, 85.9 mmol) (**2**), pyridine (12.83 g, 162.2 mmol),  $p$ -toluenesulfonyl chloride (23.42 g, 122.8

mmol) and chloroform (80 mL), 4-Chlorobutyl-4-methylbenzenesulfonate (**4**) was prepared according to the general procedure. The reaction was completed in 2.5 h (monitored by TLC). The reaction was then quenched with ether (200 mL) and water (60 mL).

Yield: 17.86 g, 85.2%; B. P. = 173 °C / .05Torr

IR (neat): 2961, 1598, 1358, 1189, 1176, 1097, 934 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.79 (2H, d, J = 8 Hz, ArH), 7.36 (2H, d, J = 8 Hz, ArH), 4.06 (2H, -CH<sub>2</sub>OSO<sub>2</sub>Cl), 3.5 (2H, -CH<sub>2</sub>Cl), 2.45 (3H, s, ArCH<sub>3</sub>), 1.82 (4H, m, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-).

<sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ 145.1, 133.0, 130.1, 128.0, 69.7, 44.2, 28.6, 26.4, 21.8.

Anal. Calcd for C<sub>11</sub>H<sub>15</sub>SO<sub>3</sub>Cl: C, 50.28; H, 5.75. Found: C, 50.34; H, 6.06.

**General Procedure for Alkynylation of ω-Haloalkyl Tosylates:** To a cold THF solution (-70 °C) of ω-haloalkyl/cycloalkyl alkyne (1.1 equivalent) was added n-BuLi (2.5M solution in hexane, 1 equivalent) drop-wise during a period of 30 minutes. The solution was allowed to warm to room temperature. A solution of ω-haloalkyl tosylates (0.96 equivalent) in THF was added to the reaction flask followed by tetrabutylammonium iodide (10 mole %). The reaction mixture was warmed to 70 °C for 2-3 hr which turned the reaction mixture thick. The reaction mixture was monitored by GC & TLC for consumption of ω-haloalkyl tosylates. The reaction mixture was then cooled to 0 °C, quenched with saturated NH<sub>4</sub>Cl and extracted with ether (30 mL x 3). The ether layer was sequentially washed with water till the water layer was neutral, followed by additions of aqueous potassium thiosulfate, and brine. It was then dried over anhydrous MgSO<sub>4</sub>. The liquid obtained after removal of ether, was purified by Kugelrohr or by freeze-thaw distillation.

**1, 8-Dichlorooct-4-yne (9):** The general procedure was followed to prepare 8-dichlorooct-4-yne (**9**) from 5-chloro-1-pentyne (**5**, 3.61 g, 34.1 mmol), 2.5 M n-BuLi (14 mL, 35.1 mmol), 3-Chloropropyl-4-methylbenzenesulfonate (**3**, 8.50 g, 34.1 mmol), TBAI (1.26 g, 3.4 mmol) and THF (30 mL).

Yield: 4.16 g, 66%; B. P. 155 °C / 5.0 Torr

IR (neat): 2960, 2872, 2916, 1441, 1355 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.66 (4H, t, J = 6.4 Hz), 2.34 (4H, t, J = 6.8 Hz), 1.94 (4H, m).

<sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ 79.5, 44.0, 31.8, 16.4.

Anal. Calcd for C<sub>8</sub>H<sub>12</sub>Cl<sub>2</sub>: C, 53.65; H, 6.75. Found: C, 51.83; H = 6.75.

**1, 9-Dichloronon-4-yne (10):** The general procedure was adopted to synthesize **10** from 6-chlorohex-1-yne (5.42 g, 46.5 mmol), n-BuLi (2.5M solution in hexane, 16.9 mL, 42.3 mmol), 3-Chloropropyl p-Toluenesulfonate (**3**) (9.66 g, 40.2 mmol) and tetrabutylammonium iodide (1.48 g, 4.0 mmol).

Yield: 4.2 g, 56%; B.P. = 85 °C / 40 torr

IR (neat): 2957, 2868, 2844, 1434, 1291, 726 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.65 (2H, t, J = 6.4 Hz), 3.57 (2H, t, J = 6.6 Hz), 2.39-2.31 (2H, m), 2.24-2.21 (2H, m), 1.99-1.91 (2H, m), 1.91-1.83 (2H, m), 1.70-1.59 (2H, m).

<sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ 80.6, 79.0, 44.8, 44.0, 31.9, 31.8, 26.3, 18.2, 16.4.

Anal. Calcd for C<sub>9</sub>H<sub>14</sub>Cl<sub>2</sub>: C, 55.98; H, 7.31. Found: C, 56.30; H = 7.53.

**1, 10-Dichlorodec-5-yne (11):** 6-Chloro-1-hexyne (**6**, 6.45g, 55.3 mmol), n-BuLi (20 mL, 50 mmol), 4-chlorobutyl-4-methylbenzenesulfonate (**4**, 11.20 g, 45.0 mmol) and TBAI (2.48 g, 6.70 mmol) was used to synthesize **11** by adopting the general procedure. It was purified by flash chromatography.

Yield: 5.85 g, 51%; B. P. 108 °C / 30 mTorr

IR (neat): 2947, 2866, 2843, 1453, 1434, 1301, 729 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.57 (4H, t, J = 6.7 Hz), 2.20 (4H, tt, J = 7.0, 2.2 Hz), 1.94-1.84 (4H, m), 1.69-1.59 (4H, m).

<sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ 80.2, 44.8, 31.8, 26.4, 18.3.

Anal. Calcd for C<sub>10</sub>H<sub>16</sub>Cl<sub>2</sub>: C, 57.98; H, 7.79. Found: C, 58.12; H = 7.91.

**(5-Chloropent-1-ynyl)cyclopropane (12):** Cyclopropylethyne (**7**, 0.56 g, 7.5 mmol), 2.5 M n-BuLi (2.952 mL, 7.4 mmol), 3-Chloropropyl-4-methylbenzenesulfonate (**5**, 1.74 g, 7.0 mmol) and TBAI (0.26 g, 7.4 mmol) was used to prepare **12**.

Yield: 0.80 g, 79.6%; Kugelrohr distillation 100 °C / 20-35 Torr

IR (neat) 3093, 3011, 2960, 1434, 1362, 1291, 1052, 1040, 1027, 880, 812 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.63 (2H, t, J = 6.4 Hz), 2.31 (2H, t, J = 6.8 Hz), 1.91 (2H, m), 1.91 (1H, m), 0.68-0.75 (2H, m), 0.57-0.64 (2H, m).

<sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ 88.6, 73.7, 44.0, 32.0, 16.4, 8.2 (2C), -0.3.

Anal. Calcd for C<sub>8</sub>H<sub>11</sub>Cl: C, 67.37; H, 7.77. Found: C, 66.61; H = 7.78.

**(6-Chlorohex-1-ynyl)cyclopropane (13):** Cyclopropyl-ethyne (**7**, 47.00 g, 22.3 mmol), 2.5M n-BuLi in solution hexane (8 mL, 20.8 mmol), 4-Chlorobutyl-4-methylbenzene-sulfonate (**4**) (5.04 g, 19.2 mmol) and TBAI (0.70 g, 1.9 mmol) were used to prepare **13** applying general procedure.

Yield: 2.19 g, 73%; Kugelrohr distillation 132 °C / 20-40 Torr

IR (neat): 3092, 3011, 2946, 2234, 1453, 1360, 1301, 1051, 1028, 812 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.56 (2H, t, J = 6.6 Hz), 2.18 (2H, dt, J = 6.9 & 1.6 Hz), 1.93-1.81 (2H, m), 1.67-1.53 (2H, m), 1.25-1.15 (1H, m), 0.75-0.55 (4H, m).

<sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ 83.9, 74.7, 44.7, 31.6, 26.2, 18.1, 8.0, -0.5.

Anal. Calcd for C<sub>9</sub>H<sub>13</sub>Cl: C, 69.00; H, 8.36. Found: C, 68.53; H = 8.45.

**(5-Chloropent-1-ynyl)cyclobutane (14):** The general procedure was applied using cyclobutyl-ethyne (**8**, 3.00 g, 37.5 mmol, 2.5M n-BuLi solution in hexane (14.76 ml, 36.9 mmol), 3-chloropropyl-4-methylbenzenesulfonate (**3**, 8.72 g, 35.1 mmol) and TBAI (1.29 g, 36.9 mmol) for the synthesis of **14**.

Yield: 3.4 g, 72%; B. P. 120 °C / 15 Torr

IR (neat): 2983, 2944, 2865, 1437, 1334, 1290, 724 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.65 (2H, t, J = 6.5 Hz), 3.03-2.91 (1H, m), 2.37 (2H, dt, J = 6.8 Hz, 2.2 Hz), 2.28-2.16 (2H, m), 2.12-1.99 (2H, m), 1.98-1.78 (4H, m).

<sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ 85.6, 79.0, 44.0, 32.0, 30.3 (2C), 25.3, 19.3, 16.5.

Anal. Calcd for C<sub>9</sub>H<sub>13</sub>Cl: C, 69.00; H, 8.36. Found: C, 68.58; H, 8.50.

**(6-Chlorohex-1-ynyl)cyclobutane (15):** Cyclobutyl-ethyne (**8**, 1.90 g, 23.7 mmol), 2.5M n-BuLi solution in hexane (9 ml, 16.6 mmol), 4-chlorobutyl-4-methylbenzenesulfonate (**4**, 6.22 g, 23.7 mmol) and n-Bu<sub>4</sub>NI (0.87 g, 2.37 mmol)

Yield: 2.83 g, 73%; Kugelrohr distillation 145 °C / 20-40 Torr.

IR (neat): 2983, 2943, 2864, 1444, 1336, 1315, 1301, 728 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.59 (2H, t, J = 6.6 Hz), 2.98 (1H, m, cyclobutyl CH), 2.28-2.18 (4H, m), 2.12-2.00 (2H, m), 1.96-1.79 (4H, m), 1.69-1.59 (2H, m).

<sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ 85.19, 80.24, 44.90, 31.80, 30.40, 26.42, 25.34, 19.33, 18.38.

Anal. Calcd for C<sub>10</sub>H<sub>15</sub>Cl: C, 70.37; H, 8.86. Found: C, 70.34; H, 8.84.

**General Procedure for Intramolecular cyclization of ω-Haloalkylated Acetylenes:** To a dry THF solution of diisopropylamine (1 equivalent) was added n-BuLi (2.5 M in hexane, 1 equivalent) at -70 °C during a period of one hour. The lithium diisopropylamide solution was brought to -10 °C over a period of time. The LDA solution was transferred

to a jacket addition funnel via cannula at 0 °C. The LDA solution was added to a stoichiometric solution of ω,ω'-dihaloalkyl/ω-haloalkyl alkynes in dry THF at -70 °C during 45 minutes. The reaction mixture was allowed to warm up to 0 °C when the GC indicated the completion of the reaction. The reaction mixture was poured into saturated aqueous NH<sub>4</sub>Cl solution. The mixture was subsequently extracted with n-pentane. The organic layer was then washed sequentially with 2% aqueous HCl, aqueous NaHCO<sub>3</sub>, water till aqueous layer was neutral (pH ≈ 7) and finally brine solution. The organic layer was then dried over anhydrous MgSO<sub>4</sub>. The liquid obtained after removal of solvent was subjected to freeze-thaw distillation.

#### 1,2-Dicyclopropylethyne (16):

**From 1,8-Dichloro-4-Octyne (9):** The lithium diisopropylamide solution was prepared from diisopropylamine (13.90 g, 19.3 mL, 137.4 mmol), n-BuLi (2.5 M in hexane, 55.0 mL, 137.5 mmol) at -70 °C. General procedure was followed using 1,8-dichloro-4-octyne (**9**, 6.00 g, 33.5 mmol) for intramolecular cyclization to furnish **16**.

Yield: 3.2 g, 92%; Freeze-thaw distillation at 0.02 Torr

**From (5-chloropent-1-ynyl)cyclopropane (12):** The lithium diisopropylamide solution was prepared from diisopropylamine (6.32 g, 8.8 mL, 62.5 mmol) and n-BuLi (2.5 M in hexane, 25.0 mL, 62.5 mmol) at -70 °C. General procedure was adopted to synthesize **16** from 1-cyclopropyl-5-chloro-1-pentyne (2.85 g, 20.0 mmol). 80 °C/50 milibar.

Yield: 1.8 g, 85%; Freeze-thaw distillation at 0.02 Torr

IR (neat): 3092, 3012, 1425, 1377, 1216, 1051, 1002, 829, 811 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.21-1.12 (m, 2H), 0.71-0.63 (4H, m), 0.63-0.

<sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ 78.93, 8.21, -0.30.

Anal. Calcd for C<sub>8</sub>H<sub>10</sub>: C, 90.51; H, 9.49. Found: C, 89.61; H, 9.49.

**(Cyclopropylethynyl)cyclobutane (17):** The lithium diisopropylamide solution was prepared from diisopropylamine (6.32 g, mL, 62.5 mmol) and n-BuLi (2.5 M in hexane, 25.0 mL, 62.5 mmol) at -70 °C. The synthesis of **17** from 1-(5-Chloropent-1-ynyl)cyclobutane (**14**) (3.13 g, 20.0 mmol), was carried out according to the general procedure to synthesize).

Yield: 1.80 g, 75%; Freeze-thaw distillation;

IR (neat): 3092, 2982, 2944, 2865, 1363, 1050, 1026, 976, 909, 810 cm<sup>-1</sup>.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.01-2.90 (1H, m), 2.26-2.15 (2H, m), 2.12-1.99 (2H, m), 1.94-1.77 (2H, m), 1.30-1.18 (1H, m), 0.76-0.69 (2H, m), 0.65-0.59 (2H, m).

<sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): δ 84.22, 79.89, 30.41 (2C, CH<sub>2</sub>), 25.38, 19.27, 8.35 (2C, CH<sub>2</sub>), -0.18;

Anal. Calcd for C<sub>9</sub>H<sub>12</sub>: C, 89.94; H10.06. Found: C, 89.90; H, 10.07.

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